

Debye–Hückel theory for two-dimensional Coulomb systems living on a finite surface without boundaries

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Abstract

We study the statistical mechanics of a multicomponent two-dimensional Coulomb gas which lives on a finite surface without boundaries. We formulate the Debye–Hückel theory for such systems, which describes the low-coupling regime. There are several problems, which we address, to properly formulate the Debye–Hückel theory. These problems are related to the fact that the electric potential of a single charge cannot be defined on a finite surface without boundaries. One can only define properly the Coulomb potential created by a globally neutral system of charges. As an application of our formulation, we study, in the Debye–Hückel regime, the thermodynamics of a Coulomb gas living on a sphere of radius R . We find, in this example, that the grand potential (times the inverse temperature) has a universal finite-size correction $(1/3)\ln R$. We show that this result is more general: for any arbitrary finite geometry without boundaries, the grand potential has a finite-size correction $(\chi/6)\ln R$, with χ the Euler characteristic of the surface and R^2 its area.

Key words: Two-dimensional Coulomb gas, Debye–Hückel theory, sphere
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1 Motivation

In this paper, we study two-dimensional Coulomb systems, for instance plasmas or electrolytes, which live on a finite surface without boundaries. The sim-

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plest example of such geometry is the sphere. This kind of geometry has been used in numerical simulations of charged systems [1,2,3,4] as an alternative to the Ewald method, since it avoids the problem of the boundary conditions. There has been also several theoretical studies of Coulomb systems on the sphere, in particular, the statistical mechanics of both the one-component plasma and the charge symmetric two-component plasma, can be exactly solved for a special value of the Coulomb coupling [5,6,7]. The purpose of this work is to formulate the Debye–Hückel theory for a generic multi-component Coulomb system living on a surface without boundaries. The Debye–Hückel theory describes the low-coupling regime of the system.

There are several difficulties which make this problem non-trivial. First, it is not possible to define the Coulomb potential as the inverse of the Laplacian operator, since on a surface without boundaries, the Laplacian has no inverse. Physically, this means that the electric potential of a single charge, on the sphere, does not exist. One can only properly define the electric potential created by a globally neutral configuration of charges. Thus, the partition function of such system should be restricted to neutral configurations. This problem is not present on an infinite surface, or a surface with boundaries, where any excess charge can go to infinity or to the boundaries, and does not affect the bulk thermodynamics of the system.

There are several equivalent ways to formulate the Debye–Hückel theory. Recently, the author and a collaborator proposed one, which is particularly appropriate to study confined Coulomb systems [8,9]. This method is based on the Hubbard–Stratonovich transformation, also known as the sine-Gordon transformation, when applied to Coulomb systems. However, for a Coulomb system living in a surface without boundary, this method is not directly applicable, because: 1) to use the sine-Gordon transformation one should consider all possible configurations of the system, including the globally charged ones, 2) the Laplacian, which in a flat geometry appears as the inverse of the Coulomb potential, has no inverse on a surface without boundaries.

The outline of this work is as follows. In the next section, we will show how to overcome the difficulties mentioned above and how the approach of Refs. [8,9] can be extended to geometries without boundaries. For simplicity we will consider the case of the sphere, however the method presented in Sec. 2 is general enough to be applicable to any surface without boundaries. In Sec. 3, using the results of Sec. 2, we will explicitly compute the grand potential and other thermodynamics functions of a Coulomb system living on a sphere in the Debye–Hückel regime. We will also compute the finite-size expansion of the grand potential, and show the existence of a finite-size correction $(1/3) \ln R$ to the grand potential (times the reduced inverse temperature), where R is the radius of the sphere. Finally in Sec. 4, with the aid of some results from Ref. [9], we will show that for a general geometry without boundaries, the

grand potential has a logarithmic finite-size correction $(\chi/6) \ln R$ where χ is the Euler characteristic of the manifold where the system lives and R^2 is proportional to the area of the manifold.

2 Modified sine-Gordon transformation

2.1 Coulomb potential and energy of a pair of pseudocharges

The Coulomb potential is usually defined as the solution of Poisson equation

$$\Delta v(\mathbf{r}, \mathbf{r}') = -2\pi \delta(\mathbf{r}, \mathbf{r}') \quad (2.1)$$

with appropriate boundary conditions. For a flat plane geometry, the potential is

$$v^0(\mathbf{r}, \mathbf{r}') = -\ln \frac{|\mathbf{r} - \mathbf{r}'|}{L} \quad (2.2)$$

which satisfies (2.1) and the boundary condition $\nabla v^0(\mathbf{r}, \mathbf{r}') \rightarrow 0$ as $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$. In equation (2.2), L is an arbitrary constant which fixes the zero of the electric potential.

On a sphere, of radius R , and more generally on any finite surface without boundaries, it is not possible to define the Coulomb potential from Poisson equation (2.1). This equation has no solution on the sphere: the electric potential of a single charge cannot be defined. Instead, following [3], we should consider that the system is composed of pseudocharges. A pseudocharge is the combination a unit point charge and a uniform background of opposite charge spread over the sphere. The electric potential v created by a unit pseudocharge satisfies

$$\Delta v(\tilde{\Omega}, \tilde{\Omega}') = -2\pi \left(\delta(\tilde{\Omega}, \tilde{\Omega}') - \frac{1}{4\pi R^2} \right). \quad (2.3)$$

with $\tilde{\Omega} = (\theta, \varphi)$ the spherical coordinates of source and $\tilde{\Omega}' = (\theta', \varphi')$ the location where the potential is computed, and $\delta(\tilde{\Omega}, \tilde{\Omega}') = \delta(\cos \theta - \cos \theta') \delta(\varphi - \varphi')/R^2$ is the Dirac distribution on the sphere of radius R .

Decomposing in spherical harmonics $Y_{\ell m}$, one can write down the solution of the previous equation as

$$v(\tilde{\Omega}; \tilde{\Omega}') = 2\pi \sum_{\ell=1}^{\infty} \sum_{m=-\ell}^{\ell} \frac{1}{\ell(\ell+1)} \overline{Y_{\ell m}(\theta', \varphi')} Y_{\ell m}(\theta, \varphi) + V_0 \quad (2.4)$$

with V_0 an arbitrary constant. Now, using [10]

$$-\ln \sin \frac{\vartheta}{2} = \sum_{\ell=1}^{\infty} \frac{2\ell+1}{2\ell(\ell+1)} P_{\ell}(\cos \vartheta) + \frac{1}{2} \quad (2.5)$$

where $P_\ell(x)$ are the Legendre polynomials of order ℓ , and ϑ is the angle between $\tilde{\Omega}$ and $\tilde{\Omega}'$, we can write the Coulomb potential (2.4) as

$$v(\theta, \varphi; \theta', \varphi) = -\ln \sin \frac{\vartheta}{2} - \frac{1}{2} + V_0. \quad (2.6)$$

The potential energy E_{ij} of two pseudocharges q_i and q_j located at $\tilde{\Omega}_i$ and $\tilde{\Omega}_j$ can be decomposed as $E_{ij} = V_{ij} + \varepsilon_i + \varepsilon_j$, with V_{ij} the interaction energy and ε_i (ε_j) the self-energy of the pseudocharge q_i (q_j). The interaction energy is

$$V_{ij} = q_i \int v(\tilde{\Omega}_i, \tilde{\Omega}) \rho_j(\tilde{\Omega}) R^2 d\tilde{\Omega} \quad (2.7)$$

where $\rho_j(\tilde{\Omega}) = q_j \delta(\tilde{\Omega}, \tilde{\Omega}_j) - q_j / (4\pi R^2)$ is the charge density of the pseudocharge q_j . We find

$$V_{ij} = -q_i q_j \left(\ln \sin \frac{\vartheta_{ij}}{2} - \frac{1}{2} \right) \quad (2.8)$$

with ϑ_{ij} the angle between $\tilde{\Omega}_i$ and $\tilde{\Omega}_j$ measured from the center of the sphere. Notice that the interaction energy does not depend on the arbitrary constant V_0 .

Following [3], the self-energy ε_i of a pseudocharge can be computed by integrating the square of the electric field $\mathbf{E}(\tilde{\Omega}) = -\nabla v(\tilde{\Omega}, \tilde{\Omega}_i)$ created by the pseudocharge on the whole sphere. However this self-energy is infinite for a point charge. Instead we can replace, initially, the point charge by a small disk of radius a with the charge q_i spread over its perimeter and we compute

$$\varepsilon_i = \frac{R^2}{4\pi} \int |\mathbf{E}(\tilde{\Omega})|^2 d\tilde{\Omega} - \varepsilon_i^s. \quad (2.9)$$

We have subtracted ε_i^s , the self-energy of the charge q_i alone, without its neutralizing background. This self-energy ε_i^s is not properly defined on the sphere, since it correspond to a non-neutral charge configuration. As in Ref. [3] we adopt the prescription of taking ε_i^s as the self-energy of the charge q_i on a flat surface

$$\varepsilon_i^s = -\frac{q_i^2}{2} \ln \frac{a}{L} \quad (2.10)$$

In the limit of a point charge, $a \rightarrow 0$, the self-energy of the pseudocharge (2.9) is finite

$$\varepsilon_i = \frac{q_i^2}{4} \left(-1 + 2 \ln \frac{2R}{L} \right). \quad (2.11)$$

Let us now study a Coulomb system on the sphere composed of several species of pseudocharges q_α , $\alpha = 1, \dots, s$. Each species α has N_α pseudocharges. The position of the i -th pseudocharge of the species α will be denoted by $\tilde{\Omega}_{\alpha,i}$. The

total potential energy of the system is

$$H = \frac{1}{2} \sum_{\alpha, \gamma} \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\gamma}{}' q_\alpha q_\gamma v_c(\tilde{\Omega}_{\alpha,i}, \tilde{\Omega}_{\gamma,j}) + \sum_{\alpha} \sum_{i=1}^N \varepsilon_\alpha \quad (2.12)$$

with

$$v_c(\tilde{\Omega}_{\alpha,i}, \tilde{\Omega}_{\gamma,j}) = -\ln \sin(\vartheta_{ij}/2) - 1/2 \quad (2.13)$$

and ϑ_{ij} the angle from the center of the sphere between $\tilde{\Omega}_{\alpha,i}$ and $\tilde{\Omega}_{\gamma,j}$. The prime in the summation in (2.12) means that the term when $\alpha = \gamma$ and $i = j$ must be omitted.

We shall call “neutral” any configuration of pseudocharges satisfying $\sum_{\alpha} q_{\alpha} N_{\alpha} = 0$. For a neutral configuration, the backgrounds of the pseudocharges cancel each other, and the system is equivalent to a system of charged particles without neutralizing backgrounds. For those neutral configurations, we have $(\sum_{\alpha} \sum_{i=1}^{N_{\alpha}} q_{\alpha})^2 = 0 = \sum_{\alpha} \sum_{i=1}^{N_{\alpha}} q_{\alpha}^2 + \sum_{\alpha, \gamma} \sum_{i=1}^{N_{\alpha}} \sum_{j=1}^{N_{\gamma}}{}' q_{\alpha} q_{\gamma}$. Then, the potential energy can be put in the form

$$H_{\text{neutral}} = -\frac{1}{2} \sum_{\alpha, \gamma} \sum_{i,j}{}' q_{\alpha} q_{\gamma} \ln \left(\frac{2R}{L} \sin \frac{\vartheta_{ij}}{2} \right). \quad (2.14)$$

In the flat limit $R \rightarrow \infty$, keeping $r_{ij} = R\vartheta_{ij}$ finite, the above expression reduces to $H_{\text{flat}} = -(1/2) \sum_{\alpha, \gamma} \sum_{i,j}{}' q_{\alpha} q_{\gamma} \ln(r_{ij}/L)$, which is the hamiltonian of a Coulomb system in the flat geometry. Thus, the prescription (2.11) for the self-energy is a reasonable one, if one wishes to recover the results for the flat geometry in the limit $R \rightarrow \infty$ [4]. Notice, however, that the thermodynamics of the Coulomb system on the flat geometry can only be recovered if we consider only neutral configurations from the start on the sphere.

2.2 Sine-Gordon transformation

We shall work in the grand canonical ensemble. The fugacity of the species α will be denoted by ζ_{α} . We define as usual $\beta = 1/(k_B T)$, where T is the absolute temperature and k_B is the Boltzmann constant. The grand partition function reads

$$\Xi = \sum_{N_1=0}^{\infty} \cdots \sum_{N_s=0}^{\infty} \delta_{\sum_{\alpha} q_{\alpha} N_{\alpha}, 0} \frac{\zeta_1^{N_1} \cdots \zeta_s^{N_s}}{N_1! \cdots N_s!} \int \cdots \int e^{-\beta H} \prod_{\alpha=1}^r \prod_{i=1}^{N_{\alpha}} R^2 d\tilde{\Omega}_{\alpha,i} \quad (2.15)$$

The Kronecker symbol $\delta_{\sum_{\alpha} q_{\alpha} N_{\alpha}, 0}$ ensures that we only take neutral configurations.

Introducing the charge density $\rho(\tilde{\Omega}) = \sum_{\alpha,i} q_{\alpha} \delta(\tilde{\Omega} - \tilde{\Omega}_{\alpha,i})$, the hamiltonian (2.12)

can be put in the form

$$H = \frac{1}{2} \int \rho(\tilde{\Omega}) \rho(\tilde{\Omega}') v_c(\tilde{\Omega}, \tilde{\Omega}') R^2 d\tilde{\Omega} R^2 d\tilde{\Omega}' + \sum_{\alpha, i} \left[\varepsilon_\alpha - \frac{q_\alpha^2}{2} v_c(\tilde{\Omega}_{\alpha, i}, \tilde{\Omega}_{\alpha, i}) \right] \quad (2.16)$$

The term $v_c(\tilde{\Omega}_{\alpha, i}, \tilde{\Omega}_{\alpha, i})$ which is subtracted corresponds to the term when, for the same particle, $\tilde{\Omega} = \tilde{\Omega}'$ in the integral which should not be included in the hamiltonian. Using the explicit expression of the self energy (2.11), we notice that $\varepsilon_\alpha - q_\alpha^2 v_c(\tilde{\Omega}_{\alpha, i}, \tilde{\Omega}_{\alpha, i})/2 = -q_\alpha^2 v^0(\mathbf{r}_{\alpha, i}, \mathbf{r}_{\alpha, i})/2$ is the self-energy of a particle in the flat geometry.

Let us decompose the hamiltonian in spherical harmonics $Y_{\ell m}$. Let

$$\rho(\tilde{\Omega}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \rho_{\ell m} Y_{\ell m}(\tilde{\Omega}). \quad (2.17)$$

Using (2.4) we have

$$H = \pi R^4 \sum_{\ell=1}^{\infty} \sum_{m=-\ell}^{\ell} \frac{|\rho_{\ell m}|^2}{\ell(\ell+1)} - \sum_{\alpha, i} q_\alpha^2 v^0(\mathbf{r}_{\alpha, i}, \mathbf{r}_{\alpha, i})/2. \quad (2.18)$$

There are two problems to proceed to apply the sine-Gordon transformation to the grand partition function. First, the potential v_c from equation (2.13), has no inverse. This can be seen in the expansion in spherical harmonics given by equation (2.4), with the term for $\ell = 0$, $V_0 = 0$. Second, to apply the sine-Gordon transformation one needs to consider all configurations of the system including the non-neutral ones. However, both problems are related and can be solved jointly.

Let us write $\delta_{\sum_\alpha q_\alpha N_\alpha, 0} = \lim_{\epsilon \rightarrow \infty} \exp \left[-\beta \epsilon (\sum_\alpha q_\alpha N_\alpha)^2 / 4 \right]$ in the partition function (2.15). Then we have $\Xi = \lim_{\epsilon \rightarrow \infty} \Xi_\epsilon$, where Ξ_ϵ is a partition function not restricted to neutral configurations and with hamiltonian

$$H_\epsilon = H + \epsilon \left[\sum_\alpha q_\alpha N_\alpha \right]^2 / 4. \quad (2.19)$$

This last term can be seen as a $\ell = 0$ component to the interaction between pairs of particles. Indeed, since $\rho_{00} = R^{-2} \sum_{\alpha, i} q_\alpha Y_{00}(\Omega_{\alpha, i}) = (4\pi)^{-1/2} R^{-2} \sum_\alpha q_\alpha N_\alpha$, we have

$$H_\epsilon = \pi R^4 \left[\rho_{00}^2 \epsilon + \sum_{\ell=1}^{\infty} \sum_{m=-\ell}^{\ell} \frac{|\rho_{\ell, m}|^2}{\ell(\ell+1)} \right] - \sum_{\alpha, i} q_\alpha^2 v^0(\mathbf{r}_{\alpha, i}, \mathbf{r}_{\alpha, i})/2. \quad (2.20)$$

This solves also the second problem we faced before to apply the sine-Gordon transformation: the quadratic form in the hamiltonian has now a non-vanishing

$\ell = 0$ term and it is now invertible. At the end of the calculations we should take $\epsilon \rightarrow \infty$. Thus, the $\ell = 0$ term of (2.20) goes to infinity. If we remember that the Coulomb potential is the inverse of the Laplacian operator, this is a reminder that $1/[\ell(\ell + 1)]$ diverges when $\ell = 0$. This $\ell = 0$ term that we naturally introduce to take into account only the neutral configurations, has also modified the pair potential to render it invertible. Its inverse is the Laplacian, plus a $\ell = 0$ component proportional to $1/\epsilon$.

We now proceed as usual and perform the sine-Gordon transformation. In Refs. [8,9] we showed that the role of the flat self-energy term v^0 in (2.20) is to regularize the ultraviolet divergence of the other terms. Therefore we will concentrate our efforts only in the part $H'_\epsilon = \pi R^4 [\rho_{00}^2 \epsilon + \sum_{\ell=1}^{\infty} \sum_{m=-\ell}^{\ell} |\rho_{\ell,m}|^2 / [\ell(\ell + 1)]]$. Performing the sine-Gordon transformation [11], we have

$$\Xi_\epsilon = \frac{Z}{Z_0} = \frac{\int \prod_{\ell=0}^{\infty} \prod_{m=-\ell}^{\ell} d\phi_{\ell m} \exp[-S(\{\zeta_\alpha\})]}{\int \prod_{\ell=0}^{\infty} \prod_{m=-\ell}^{\ell} d\phi_{\ell m} \exp[-S(0)]} \quad (2.21)$$

with the action

$$S(\{\zeta_\alpha\}) = -\frac{1}{2} \sum_{\ell,m} A_{\ell m} \phi_{\ell m}^2 - \sum_{\alpha} \zeta_{\alpha} \int :: \exp \left[-i\beta q_{\alpha} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \phi_{\ell m} Y_{\ell m}(\tilde{\Omega}) \right] :: R^2 d\tilde{\Omega}. \quad (2.22)$$

We have defined $A_{\ell m} = \beta \ell(\ell + 1)/(2\pi)$ if $\ell \geq 1$ and $A_{00} = \beta \epsilon/(2\pi)$. ($A_{\ell m}$) represents an operator which is the inverse of the modified Coulomb potential. It is proportional to the Laplacian plus a $\ell = 0$ component. $\phi(\tilde{\Omega}) = \sum_{\ell,m} \phi_{\ell m} Y_{\ell m}(\tilde{\Omega})$ is the traditional auxiliary field introduced in the sine-Gordon transformation. The notation $:: \dots ::$ is defined as

$$:: e^{-i\beta q_{\alpha} \phi(\tilde{\Omega})} :: = e^{-i\beta q_{\alpha} \phi(\tilde{\Omega})} e^{\beta q_{\alpha}^2 v^0(\mathbf{r}, \mathbf{r})} \quad (2.23)$$

with $\mathbf{r} = (R, \tilde{\Omega})$, and can be understood as a sort of normal ordering operator, for details see [12].

The $\ell = 0$ term in the action S is special, because at the end we will be interested in the limit $\epsilon \rightarrow \infty$. Let us do the change of variable in the functional integral $X = \sqrt{\beta/(2\pi\epsilon)} \phi_{00}$. The action is now

$$S(\{\zeta_\alpha\}) = \sum_{\ell \geq 1, m} \frac{\beta \ell(\ell + 1)}{4\pi} \phi_{\ell m}^2 + \frac{X^2}{2} - \sum_{\alpha} \zeta_{\alpha} \int :: e^{-i\beta q_{\alpha} [\sum_{\ell \geq 1, m} \phi_{\ell m} Y_{\ell m}(\tilde{\Omega}) + \sqrt{\epsilon/(2\beta)} X]} :: R^2 d\tilde{\Omega}. \quad (2.24)$$

2.3 Steepest descent

We now consider the low-coupling or Debye–Hückel regime, when $\beta e^2 \ll 1$, with e the elementary charge (all charges $q_\alpha = z_\alpha e$ are supposed to be multiples of e , $z_\alpha \in \mathbb{Z}$). In the low-coupling approximation, the action (2.24) is expanded to the quadratic order around the solution of the stationary action equation $\delta S/\delta\phi = 0$, then the functional integral in equation (2.21) is Gaussian and can be performed exactly. The stationary action equation $\delta S/\delta\phi = 0$ reads, for $\ell \geq 1$,

$$\frac{\beta}{2\pi} \ell(\ell+1) \phi_{\ell m} + \sum_{\alpha} i\beta q_{\alpha} \zeta_{\alpha} \int Y_{\ell m}(\tilde{\Omega}) e^{-i\beta q_{\alpha} \left[\sum_{\ell \geq 1, m} \phi_{\ell m} Y_{\ell m}(\tilde{\Omega}) + \sqrt{\epsilon/(2\beta)} X \right]} R^2 d\tilde{\Omega} = 0 \quad (2.25)$$

and, for $\ell = 0$,

$$X + \sum_{\alpha} i\beta q_{\alpha} \zeta_{\alpha} \sqrt{\frac{\epsilon}{2\beta}} \int e^{-i\beta q_{\alpha} \left[\sum_{\ell \geq 1, m} \phi_{\ell m} Y_{\ell m}(\tilde{\Omega}) + \sqrt{\epsilon/(2\beta)} X \right]} R^2 d\tilde{\Omega} = 0 \quad (2.26)$$

Since the system is homogeneous and isotropic, we look for a constant solution, $\phi_{\ell m} = 0$ for $\ell \geq 1$, which naturally satisfies (2.25). Then equation (2.26) reduces to

$$\frac{X}{2\pi\sqrt{2\beta\epsilon}} + iR^2 \sum_{\alpha} q_{\alpha} \zeta_{\alpha} e^{-i\beta q_{\alpha} \sqrt{\epsilon/(2\beta)} X} = 0 \quad (2.27)$$

Since we are interested in the limit $\epsilon \rightarrow \infty$, the first term can be neglected and we have

$$\sum_{\alpha} q_{\alpha} \zeta_{\alpha} e^{-i\beta q_{\alpha} \sqrt{\epsilon/(2\beta)} X} = 0 \quad (2.28)$$

Notice that, if the fugacities are chosen to satisfy the pseudoneutrality condition $\sum_{\alpha} q_{\alpha} \zeta_{\alpha} = 0$, then $X = 0$ is a solution of (2.28). But $X = X_n = n2\pi\sqrt{2/(\beta e^2 \epsilon)}$ is also a solution with $n \in \mathbb{Z}$. Contrary to the usual situation in the infinite geometry or geometries with boundaries [8,9] when only the $\phi = 0$ stationary solution contributes, here all stationary solutions contribute to the functional integral (2.21), since when $\epsilon \rightarrow \infty$, all $X_n \rightarrow 0$.

Let us proceed more generally, supposing that the fugacities are arbitrary and do not necessarily satisfy the pseudoneutrality condition. Let $\psi_0 \in \mathbb{R}$ be the solution of

$$\sum_{\alpha} q_{\alpha} \zeta_{\alpha} e^{-\beta q_{\alpha} \psi_0} = 0, \quad (2.29)$$

which is unique since the l.h.s. of (2.29) is a monotonous function of ψ_0 . Let us define $\zeta_{\alpha}^* = \zeta_{\alpha} e^{-\beta q_{\alpha} \psi_0}$. These “renormalized” fugacities satisfy the pseudoneutrality condition $\sum_{\alpha} \zeta_{\alpha}^* q_{\alpha} = 0$. Clearly the general solutions to equation (2.28) are

$$X_n = 2\pi n \sqrt{\frac{2}{\beta e^2 \epsilon}} + X_0, \quad n \in \mathbb{Z} \quad (2.30)$$

with $X_0 = -i\sqrt{(2\beta/\epsilon)}\psi_0$. Now, we proceed to apply the steepest descent method to evaluate (2.21). Notice that it is valid to apply this method when $\beta e^2 \ll 1$ and $\zeta_\alpha R^2 \gg 1$. This last condition is necessary for the part of the integral depending on X . Taking into account all the stationary points X_n we have

$$\begin{aligned} \Xi_\epsilon = \frac{1}{Z_0} \sum_{n \in \mathbb{Z}} \int \prod_{\ell \geq 1, m} d\phi_{\ell m} dX e^{-\frac{\beta}{\epsilon} \left(\frac{2\pi n}{\beta e} - i\psi_0 \right)^2 + 4\pi R^2 \sum_\alpha \zeta_\alpha^*} \\ \times \exp \left[-\frac{\beta}{4\pi} \sum_{\ell \geq 1, m} [\ell(\ell+1) + (\kappa R)^2] :: \phi_{\ell m} ::^2 - \frac{1}{2} (1 + \epsilon(\kappa R)^2)(X - X_n)^2 \right] \end{aligned} \quad (2.31)$$

with $\kappa = \sqrt{2\pi\beta \sum_\alpha q_\alpha^2 \zeta_\alpha^*}$ the inverse Debye length. Performing the Gaussian integrals we find

$$\Xi_\epsilon = \left[\prod_{\ell \geq 1, m} \left(1 + \frac{(\kappa R)^2}{\ell(\ell+1)} \right) \prod_k e^{\kappa^2/\lambda_k^0} \right]^{-1/2} e^{V \sum_\alpha \zeta_\alpha^*} f(\epsilon) \quad (2.32)$$

where $\lambda_k^0 = -\mathbf{K}^2$, $\mathbf{K} \in \mathbb{R}^2$, are the eigenvalues of the Laplacian operator in the flat space \mathbb{R}^2 (these appear from the self-energy term v^0 in the hamiltonian, for details see [8,9,12]), and $V = 4\pi R^2$ is the total area of the sphere. In the previous equation we have defined

$$f(\epsilon) = (1 + (\kappa R)^2 \epsilon)^{-1/2} \sum_{n \in \mathbb{Z}} e^{-\frac{\beta}{\epsilon} \left(\frac{2\pi n}{\beta e} - i\psi_0 \right)^2} \quad (2.33)$$

which can be expressed in terms of the Jacobi function $\vartheta_3(u|\tau) = \sum_{n \in \mathbb{Z}} e^{i\pi\tau n^2 + 2\pi n u i}$ as

$$f(\epsilon) = (1 + (\kappa R)^2 \epsilon)^{-1/2} e^{\beta\psi_0^2/\epsilon} \vartheta_3 \left(\frac{2\pi\psi_0}{e\epsilon} \middle| \frac{4\pi i}{\beta e^2 \epsilon} \right) \quad (2.34)$$

To compute the limit of Ξ_ϵ when $\epsilon \rightarrow \infty$, it is useful to use the Jacobi imaginary transformation [13] to express $f(\epsilon)$ as

$$f(\epsilon) = \sqrt{\frac{\beta e^2 \epsilon}{4\pi(1 + (\kappa R)^2 \epsilon)}} \vartheta_3 \left(\frac{\beta e \psi_0}{2} \middle| \frac{i\beta e^2 \epsilon}{4\pi} \right). \quad (2.35)$$

The last term, the ϑ_3 function, has limit 1 when $\epsilon \rightarrow \infty$. Finally, taking $\epsilon \rightarrow \infty$ we obtain the original partition function of the Coulomb system in the sphere

$$\Xi = \left[\frac{4\pi}{\beta e^2} (\kappa R)^2 \prod_{\ell \geq 1, m} \left(1 + \frac{(\kappa R)^2}{\ell(\ell+1)} \right) \prod_k e^{\kappa^2/\lambda_k^0} \right]^{-1/2} e^{V \sum_\alpha \zeta_\alpha^*}. \quad (2.36)$$

It should be clear to the reader that the above calculations are very general and can be easily adapted to other types of finite geometries without boundaries.

In that general case, the spherical harmonics and $-\ell(\ell+1)/R^2$ are replaced, respectively, by the eigenfunctions and the eigenvalues of the Laplacian in the considered geometry. For a finite surface without boundaries, any constant function is an eigenfunction of the Laplacian with zero eigenvalue. This constant function plays the role of Y_{00} . Thus in an arbitrary finite surface without boundaries the grand partition function of the Coulomb gas is

$$\Xi = \left[\frac{\kappa^2 V}{\beta e^2} \prod_{n, \lambda_n \neq 0} \left(1 - \frac{\kappa^2}{\lambda_n} \right) \prod_k e^{\kappa^2/\lambda_k^0} \right]^{-1/2} e^{V \sum_\alpha \zeta_\alpha^*}. \quad (2.37)$$

where λ_n are the eigenvalues of the Laplacian in the manifold where the system lives and V is the volume (area) of the manifold. The result is similar to the one for a geometry with boundaries and Dirichlet boundary conditions, found in Ref. [8], except that it appears an additional term $\kappa^2 V/(\beta e^2)$ which is the contribution of the zero eigenvalue.

Notice that the role of the mean field ψ_0 is to renormalize the fugacities, and the partition function is expressed in term of the fugacities ζ_α^* which satisfy the pseudoneutrality condition. We recover the fact that the fugacities are not independent controlling variables, this is due to the global neutrality of the system, which we imposed from the start. The same situation arises in geometries with boundaries, for details see the appendix B of Ref. [8].

3 Thermodynamics of a Coulomb system on a sphere in the Debye–Hückel regime

3.1 Grand potential

In this section we consider the sphere geometry and we compute explicitly the partition function (2.36). The results of this section are specific to the sphere.

The grand potential $\Omega = -k_B T \ln \Xi$ is given by

$$\begin{aligned} \beta\Omega = & \frac{1}{2} \ln \frac{4\pi(\kappa R)^2}{\beta e^2} + \frac{1}{2} \ln \prod_{\ell=1}^N \left(1 + \frac{R^2 \kappa^2}{\ell(\ell+1)} \right)^{2\ell+1} - (\kappa R)^2 \int_{k_{\min}}^{K_{\max}} \frac{dK}{K} \\ & - \sum_{\alpha} V \zeta_{\alpha}^* \end{aligned} \quad (3.1)$$

The integral term in equation (3.1) comes from the eigenvalues λ_k^0 of the Laplacian in the flat space. The infinite product in equation (3.1) is divergent for large ℓ and it should be cutoff to a maximum value N of ℓ . This ultraviolet

divergence is compensated by the one from the integral when $K_{\max} \rightarrow \infty$. As explained and illustrated in several examples in Refs. [8,9], the cutoffs K_{\max} and N are proportional and the exact relation between them can be found by requiring that in the limit $R \rightarrow \infty$ we recover the bulk grand potential in the flat space which is known. In the integral we also need to introduce an infrared cutoff k_{\min} . It is explained in Refs. [8,9] that this cutoff is $k_{\min} = 2e^{-C}/L$, where C is the Euler constant. The length L is the same from equation (2.2) which appears in the flat Coulomb potential v^0 . In the Debye–Hückel regime it is understood that L is large, $L \rightarrow \infty$.

We can obtain an explicit expression for a certain regularization of the infinite product appearing in (3.1). Let us consider the infinite product

$$P(z) = \prod_{\ell=1}^{\infty} \left(1 + \frac{z^2}{\ell(\ell+1)}\right)^{\ell} e^{-z^2/\ell} \quad (3.2)$$

which is convergent. Let us introduce the Barnes G function [14,15]

$$G(z+1) = (2\pi)^{z/2} e^{-z(z+1)/2 - Cz^2/2} \prod_{\ell=1}^{\infty} \left(1 + \frac{z}{\ell}\right)^{\ell} e^{-z+z^2/(2\ell)} \quad (3.3)$$

with C the Euler constant. Let us write in equation (3.2)

$$1 + \frac{z^2}{\ell(\ell+1)} = \frac{\left(1 - \frac{\nu_1}{\ell}\right)\left(1 - \frac{\nu_2}{\ell}\right)}{\left(1 + \frac{1}{\ell}\right)} \quad (3.4)$$

with

$$\nu_{1,2} = \left(-1 \pm \sqrt{1 - 4z^2}\right)/2 \quad (3.5)$$

that satisfy $\ell(\ell+1) + z^2 = (\ell - \nu_1)(\ell - \nu_2)$. This allow us to express the product $P(z)$ in terms of the Barnes G function, generalizing a standard procedure used to express infinite products in terms of Gamma functions [13],

$$P(z) = \prod_{\ell=1}^{\infty} \left(1 + \frac{z^2}{\ell(\ell+1)}\right)^{\ell} e^{-z^2/\ell} = G(1 - \nu_1)G(1 - \nu_2) e^{-(1+C)z^2} \quad (3.6)$$

Then we have

$$\prod_{\ell=1}^{\infty} \left(1 + \frac{z^2}{\ell(\ell+1)}\right)^{2\ell+1} e^{-2z^2/\ell} = \frac{[G(1 - \nu_1)G(1 - \nu_2)]^2 e^{-2(1+C)z^2}}{\Gamma(1 - \nu_1)\Gamma(1 - \nu_2)} \quad (3.7)$$

Using $\Gamma(\frac{1}{2} + x)\Gamma(\frac{1}{2} - x) = \pi / \cos(\pi x)$ and $G(1 + z) = \Gamma(z)G(z)$ we finally have

$$\prod_{\ell=1}^{\infty} \left(1 + \frac{z^2}{\ell(\ell+1)}\right)^{2\ell+1} e^{-2z^2/\ell} = \frac{\pi [G(-\nu_1)G(-\nu_2)]^2 e^{-2(1+C)z^2}}{z^2 \cosh([\pi\sqrt{4z^2 - 1}]/2)} \quad (3.8)$$

Putting $z = \kappa R$ and replacing (3.8) into the expression (3.1) for the grand potential yields

$$\begin{aligned} \beta\Omega = & \frac{1}{2} \ln \frac{4\pi(\kappa R)^2}{\beta e^2} + \frac{1}{2} \ln \frac{\pi[G(-\nu_1)G(-\nu_2)]^2}{(\kappa R)^2 \cosh([\pi\sqrt{(2\kappa R)^2 - 1}]/2)} \\ & + (\kappa R)^2 \left(-1 - C + \sum_{\ell=1}^N \frac{1}{\ell} - \ln \frac{K_{\max}}{k_{\min}} \right) - V \sum_{\alpha} \zeta_{\alpha} \end{aligned} \quad (3.9)$$

In the limit where the ultraviolet cutoffs K_{\max} and N go to infinity and replacing $k_{\min} = 2e^{-C}/L$, we have

$$\begin{aligned} \beta\Omega = & \frac{1}{2} \ln \frac{4\pi}{\beta e^2} + \frac{1}{2} \ln \frac{\pi[G(-\nu_1)G(-\nu_2)]^2}{\cosh([\pi\sqrt{(2\kappa R)^2 - 1}]/2)} \\ & + (\kappa R)^2 \left(-1 + \ln \frac{N}{K_{\max}R} + \ln \frac{2e^{-C}R}{L} \right) - V \sum_{\alpha} \zeta_{\alpha}^*. \end{aligned} \quad (3.10)$$

We see that if the ultraviolet cutoffs N and K_{\max} are proportional the expression for the grand potential is well defined. Furthermore, in the limit $R \rightarrow \infty$ we should recover the bulk value [8]

$$\frac{\beta\Omega_b}{V} = \frac{\kappa^2}{4\pi} \left[-\ln \frac{\kappa L}{2} - C + \frac{1}{2} \right] - \sum_{\alpha} \zeta_{\alpha}^* \quad (3.11)$$

for the grand potential. We can compute this thermodynamic limit using the known expansion of the Barnes G function for large argument [14,15,16]

$$\ln G(1+z) \sim z^2 \left(\frac{\ln z}{2} - \frac{3}{4} \right) + \frac{z}{2} \ln(2\pi) - \frac{\ln z}{12} + \zeta'(-1) + O(1/z). \quad (3.12)$$

($\zeta'(-1)$ is the derivative of the Riemann zeta function evaluated at -1). Using this expansion we find that it is necessary that $K_{\max} = N/R$ to recover the correct bulk grand potential in the limit $R \rightarrow \infty$. Finally the grand potential for finite R can be expressed as

$$\begin{aligned} \beta\Omega = & \frac{1}{2} \ln \frac{4\pi^2[G(-\nu_1)G(-\nu_2)]^2}{\beta e^2 \cosh([\pi\sqrt{(2\kappa R)^2 - 1}]/2)} + (\kappa R)^2 \left(-1 + \ln \frac{2e^{-C}R}{L} \right) \\ & - V \sum_{\alpha} \zeta_{\alpha}^*. \end{aligned} \quad (3.13)$$

Using (3.12), we can find the finite-size expansion of the grand potential

$$\beta\Omega = \beta\Omega_b + \frac{1}{3} \ln(\kappa R) + 2\zeta'(-1) - \frac{1}{4} - \frac{1}{2} \ln \frac{\beta e^2}{4\pi} + O(1/(\kappa R)) \quad (3.14)$$

with the bulk grand potential Ω_b given by equation (3.11). This expansion for the grand potential shows that there is a finite-size logarithmic correction $(\chi/6) \ln R$, where $\chi = 2$ is the Euler characteristic of the sphere. Since the system has no boundary there is no surface (perimeter) tension term.

3.2 Densities, pressure and the equation of state

The density n_α of the species α can be obtained using the standard thermodynamic relation $n_\alpha = \zeta_\alpha \partial \ln \Xi / \partial \zeta_\alpha$. When computing this derivative one has to take into account the fact that ψ_0 is a function of ζ_α implicitly given by equation (2.29). After some long but straightforward calculation we finally find

$$n_\alpha = \zeta_\alpha^* \left[1 - \left(\frac{\beta q_\alpha^2}{2} - \frac{\pi \beta^2 q_\alpha \sum_\gamma q_\gamma^3 \zeta_\gamma^*}{\kappa^2} \right) \times \left(\psi(1 + \nu_1) + \frac{\pi}{2} \cot(\pi \nu_1) + C + \ln \frac{L}{2R} \right) \right]. \quad (3.15)$$

We have used the relation [15]

$$\ln G(1 + z) = \frac{z(1 - z)}{2} + \frac{z}{2} \ln(2\pi) + \int_0^z x \psi(x) dx \quad (3.16)$$

where $\psi(x) = d \ln \Gamma(x) / dx$ is the psi function. This relation allows us to express the derivative of the Barnes G function in terms of the psi function $\psi(x)$. Also we used some known identities [10] satisfied by the psi function, such as $\psi(\nu) + \psi(-\nu - 1) = 2\psi(\nu + 1) - [\nu(\nu + 1)]^{-1} + \pi \cot(\pi \nu)$. One can easily verify that the system is neutral $\sum_\alpha q_\alpha n_\alpha = 0$. The total density $n = \sum_\alpha n_\alpha$ is

$$n = \sum_\alpha \zeta_\alpha^* - \frac{\kappa^2}{4\pi} \left(\psi(1 + \nu_1) + \frac{\pi}{2} \cot(\pi \nu_1) + C + \ln \frac{L}{2R} \right). \quad (3.17)$$

The finite-size expansion of the densities, when $R \rightarrow \infty$, reads

$$n_\alpha = n_\alpha^b - \frac{\zeta_\alpha^b}{6(\kappa R)^2} \left(\frac{\beta q_\alpha^2}{2} - \frac{\pi \beta^2 q_\alpha \sum_\gamma q_\gamma^3 \zeta_\gamma^*}{\kappa^2} \right) \quad (3.18)$$

where the bulk density is

$$n_\alpha^b = \zeta_\alpha^* \left(1 - \left(\frac{\beta q_\alpha^2}{2} - \frac{\pi \beta^2 q_\alpha \sum_\gamma q_\gamma^3 \zeta_\gamma^*}{\kappa^2} \right) \ln \frac{\kappa L e^C}{2} \right). \quad (3.19)$$

And for the total density

$$n = n^b + \frac{1}{6} \frac{1}{4\pi R^2} \quad (3.20)$$

with $n^b = \sum_{\alpha} n_{\alpha}^b$. Thus the total number of particles $N = N_b + 1/6$, where N_b is the bulk number of particles. The $1/6$ finite-size correction to the number of particles is a consequence of the $(1/3) \ln R$ correction to the grand potential.

The pressure $p = -\partial\Omega/\partial V$ is given by

$$\beta p = \sum_{\alpha} \zeta_{\alpha}^* - \frac{\kappa^2}{8\pi} + \frac{\kappa^2}{4\pi} \left(\psi(1 + \nu_1) + \frac{\pi}{2} \cot(\pi\nu_1) + \ln \frac{Le^C}{2R} \right). \quad (3.21)$$

Using equation (3.15), and neglecting terms of higher order than βe^2 , we find the equation of state

$$\beta p = \sum_{\alpha} n_{\alpha} \left(1 - \frac{\beta q_{\alpha}^2}{4} \right). \quad (3.22)$$

We remind the reader that, from a scale invariance analysis, one can show that this equation of state is actually valid in the whole range of stability of the system of point particles, both in the flat geometry and in the sphere.

3.3 Internal energy

The excess internal energy is $U_{\text{exc}} = (\partial(\beta\Omega)/\partial\beta)_{\zeta_{\alpha}, V}$. Using (3.13), we find

$$\beta U_{\text{exc}} = -(\kappa R)^2 \left(\psi(1 + \nu_1) + \frac{\pi}{2} \cot(\pi\nu_1) + C + \ln \frac{L}{2R} \right) - \frac{1}{2} \quad (3.23)$$

We recall that $\nu_1 = (-1 + \sqrt{1 - (2\kappa R)^2})/2$.

We can derive this result (3.23) using a more traditional approach to the Debye–Hückel theory. Consider a unit pseudocharge (charge plus neutralizing background) located at the north pole. Following the usual formulation of Debye–Hückel theory, this pseudocharge is screened by a polarization cloud created by the plasma. This cloud has a charge density given by

$$\begin{aligned} \rho_{\text{pol}}(\theta, \varphi) &= \sum_{\alpha} q_{\alpha} n_{\alpha} e^{-\beta q_{\alpha} K(\theta, \varphi; 0, 0)} - \int \sum_{\alpha} q_{\alpha} n_{\alpha} e^{-\beta q_{\alpha} K(\theta', \varphi'; 0, 0)} \frac{d\tilde{\Omega}'}{4\pi} \\ &\simeq -\kappa_D^2 K(\theta, \varphi; 0, 0) + \kappa_D^2 \langle K \rangle \end{aligned} \quad (3.24)$$

where $K(\theta, \varphi; 0, 0)$ is the (mean field) electric potential created at (θ, φ) by the pseudocharge and its polarization cloud. Also $\langle K \rangle = \int K(\theta', \varphi'; 0, 0) d\tilde{\Omega}'/(4\pi)$ is the average of K over the sphere. To understand the second term in (3.24)

recall that we are dealing with pseudocharges (charges plus neutralizing background), and the polarization cloud is also made of pseudocharges. In the second line we linearized the exponentials as it is usually done in the Debye–Hückel theory and defined the inverse Debye length $\kappa_D = \sqrt{2\pi\beta \sum_{\alpha} n_{\alpha} q_{\alpha}^2}$. At the Debye–Hückel level of approximation $\kappa_D \simeq \kappa$. The potential K satisfies the modified Poisson equation

$$\Delta K = -2\pi \left(\delta - \frac{1}{4\pi R^2} + \rho_{\text{pol}}(\theta, \varphi) \right) \quad (3.25)$$

and using (3.24) we arrive at the modified Debye–Hückel equation for the sphere geometry

$$\Delta K - \kappa^2 K + \kappa^2 \langle K \rangle = -2\pi \left(\delta - \frac{1}{4\pi R^2} \right) \quad (3.26)$$

As in the case of the modified Poisson equation (2.3), we can notice that the solution of the modified Debye–Hückel equation (3.26) is determined up to an arbitrary additive constant. Indeed this can be clearly seen if we look for a solution of equation (3.26) as an expansion in spherical harmonics

$$K(\theta, \varphi; 0, 0) = \sum_{\ell=1}^{\infty} \sum_{m=-\ell}^{\ell} \frac{2\pi}{\ell(\ell+1) + (\kappa R)^2} \overline{Y_{\ell m}(0, 0)} Y_{\ell m}(\theta, \varphi) + b_0 \overline{Y_{00}(0, 0)} Y_{00}(\theta, \varphi). \quad (3.27)$$

The constant term b_0 , for $l = 0$, cannot be determined from the differential equation (3.26). Thus the average $\langle K \rangle = b_0/(4\pi)$ can be chosen arbitrarily. However as we will see below this constant term will not be needed in the following.

The excess internal energy U_{exc} can be computed from the Debye–Hückel potential K as the potential energy of the pseudocharge in the north pole, in the potential field K

$$U_{\text{exc}} = \frac{4\pi R^2}{2} \sum_{\alpha} q_{\alpha}^2 n_{\alpha} \lim_{\substack{\theta \rightarrow 0 \\ r=R\theta \rightarrow 0}} \left[\int K(\theta, \varphi; 0, 0) (\delta(\theta, \varphi; 0, 0) - 1/(4\pi R^2)) R^2 d\tilde{\Omega} + \ln \frac{r}{L} \right] \quad (3.28)$$

Notice that we subtract the self-energy $-\ln(r/L)$ corresponding to a flat geometry, in accordance to the prescription (2.10), to obtain a finite result. This kind of prescription has also been used in Ref. [17] for the derivation of the

pressure of the Coulomb gas using the Maxwell stress tensor. We have

$$U_{\text{exc}} = \frac{4\pi R^2}{2} \sum_{\alpha} q_{\alpha}^2 n_{\alpha} \lim_{\substack{\theta \rightarrow 0 \\ r=R\theta \rightarrow 0}} \left(K(\theta, \varphi; 0, 0) - \langle K \rangle + \ln \frac{r}{L} \right) \quad (3.29)$$

Thus we only need $K - \langle K \rangle$, the constant term $\langle K \rangle$ is irrelevant for the calculation of the internal energy. An explicit expression for K can be obtained by noticing that the Yukawa potential Y , which is the solution of

$$\Delta Y - \kappa^2 Y = -2\pi\delta, \quad (3.30)$$

is also a particular solution of equation (3.26) with $\langle Y \rangle = 1/(2\kappa^2 R^2)$. Therefore, Y has an expansion in spherical harmonics of the form (3.27) with $b_0 = 2\pi/(\kappa^2 R^2)$. So, the difference between K and Y is a constant equal to $-1/[2(\kappa R)^2] + \langle K \rangle$. On the other hand equation (3.30) can be solved directly since it reduces to a Legendre equation in the variable $\cos\theta$. The solution is [18]

$$Y(\theta) = -\frac{\pi}{2 \sin(\nu_1 \pi)} P_{\nu_1}(-\cos\theta) \quad (3.31)$$

with P_{ν_1} a Legendre function. Finally we find the Debye–Hückel potential for a pseudocharge located at the north pole

$$K(\theta, \varphi; 0, 0) - \langle K \rangle = -\frac{\pi}{2 \sin(\nu_1 \pi)} P_{\nu_1}(-\cos\theta) - \frac{1}{2(\kappa R)^2}. \quad (3.32)$$

As $\theta \rightarrow 0$, the Legendre function has the behavior [18]

$$P_{\nu_1}(-\cos\theta) = \frac{2 \sin(\nu_1 \pi)}{\pi} \left[\ln \sin \frac{\theta}{2} + C + \psi(1 + \nu_1) + \frac{\pi}{2} \cot(\nu_1 \pi) \right] + o(1). \quad (3.33)$$

Using this asymptotic behavior into equation (3.29) allow us to retrieve the result (3.23) for the internal energy.

4 Finite-size corrections for Coulomb systems on finite surfaces without boundaries

In this section we consider a Coulomb gas confined in an arbitrary finite surface without boundaries. We will compute the finite-size expansion of the grand potential. Let R be the square root of the total area V of the surface. Following [9], we introduce the zeta function of the Laplacian in the geometry considered,

$$Z(s, a) = \sum_{k=1}^{\infty} (a - \lambda_k)^{-s} \quad (4.1)$$

where λ_k are the eigenvalues of the Laplacian. Notice that we omit the vanishing eigenvalue $\lambda_0 = 0$ in the definition (4.1).

In Ref. [9], this zeta function is related to grand potential. We can directly transpose the calculations of Ref. [9] to the present case, taking special care of the additional contribution to the grand potential due to the vanishing eigenvalue. Then, we obtain for the grand potential the relation

$$\beta\Omega = \frac{1}{2} \left[Z'(0, 0) - Z'(0, \kappa^2) \right] + \frac{\kappa^2 V}{4\pi} \ln \frac{2e^{-C}}{L} + \frac{1}{2} \ln \frac{\kappa^2 V}{\beta e^2} - V \sum_{\alpha} \zeta_{\alpha}^*. \quad (4.2)$$

The prime means differentiation with respect to first variable of the zeta function. The finite-size expansion of the zeta functions involved in (4.2) can be obtained from the known small-argument expansion of the heat kernel, $\Theta(t) = \sum_{n=0}^{\infty} e^{t\lambda_k}$, of the Laplacian [19,20] which reads,

$$\Theta(t) = \frac{V}{4\pi t} + \frac{\chi}{6} + o(t^{1/2}) \quad (4.3)$$

with χ the Euler characteristic of the surface. This is explained in detail in Ref. [9]. Here we only need to take special care of the fact that we omitted the zero eigenvalue in the zeta function, which is equivalent to subtract 1 to the heat kernel. Thus, following [9], we find

$$\frac{1}{2} \left[Z'(0, 0) - Z'(0, \kappa^2) \right] = \frac{\kappa^2}{4\pi} \left(\frac{1}{2} - \ln \kappa \right) V + \left[\frac{\chi}{6} - 1 \right] \ln(\kappa R) + O(1) \quad (4.4)$$

Replacing into (4.2) we finally find the finite-size expansion of the grand potential

$$\beta\Omega = \beta\Omega_b + \frac{\chi}{6} \ln(\kappa R) + O(1) \quad (4.5)$$

with the bulk grand potential Ω_b given by (3.11). Notice the existence of a logarithmic finite-size correction $(\chi/6) \ln R$, which is universal, i. e. independent of details of the microscopic constitution of the system. Actually this universal finite-size correction seems to exist even beyond the low-coupling regime considered here. In particular it has been shown to exist for the sphere geometry for the one-component plasma [21] and the two-component plasma both in its charge symmetric [22] and charge asymmetric version [23], in the whole range of stability of the system of point particles.

5 Summary and perspectives

We have showed how to build the Debye–Hückel theory for two-dimensional Coulomb systems confined in a finite surface without boundary. In particular we showed how to perform the sine-Gordon transformation for this kind

geometry and how to map the statistical mechanics problem into a field theory on the finite surface. This could have further applications, for instance, to compute higher order corrections in βe^2 to the grand potential and other thermodynamic quantities.

For the case of the sphere geometry we explicitly computed the grand potential and other thermodynamic quantities. For a general geometry, we showed the existence of a universal logarithmic finite-size correction for the grand potential.

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References

- [1] J. M. Caillol, D. Levesque, J. J. Weis and J. P. Hansen, *J. Stat. Phys.* **28** (1982) 325.
- [2] J. M. Caillol and D. Levesque, *Phys. Rev. B* **33** (1986) 499.
- [3] J. M. Caillol and D. Levesque, *J. Chem. Phys.* **94** (1991) 597.
- [4] J. M. Caillol, *J. Chem. Phys.* **111** (1999) 6528.
- [5] J. M. Caillol, *J. Physique-Lettres* **42** (1981) L-223.
- [6] P. J. Forrester, B. Jancovici and J. Madore, *J. Stat. Phys.* **69** (1992) 179.
- [7] G. Téllez and P. J. Forrester, *J. Stat. Phys.* **97** (1999) 489.
- [8] A. Torres and G. Téllez, *J. Phys. A: Math. Gen.* **37** (2004) 2121.
- [9] A. Torres and G. Téllez, *General Considerations on the Finite-Size Corrections for Coulomb Systems in the Debye-Hückel Regime*, e-print cond-mat/0404588, *J. Stat. Phys.* (2004), to be published.
- [10] S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1965)
- [11] S. Samuel, *Phys. Rev. D* **18** (1978) 1916.
- [12] G. Téllez, *Phys. Rev. E* **70** (2004) 011508.

- [13] E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge University Press, 1902)
- [14] E. W. Barnes, *Quart. J. Pure Appl. Math.* **31** (1900) 264.
- [15] V. S. Adamchik, *Contributions to the theory of the Barnes function*, e-print math.CA/0308086, (2003).
- [16] A. Voros, *Comm. Math. Phys.* **110** (1987) 439.
- [17] B. Jancovici, *J. Stat. Phys.* **99** (2000) 1281.
- [18] B. Jancovici, *J. Stat. Phys.* **102** (2001) 1315.
- [19] M. Kac, *Am. Math. Monthly* **73** (1966) 1.
- [20] H. P. McKean Jr and I. M. Singer, *J. Diff. Geom.* **1** (1967) 43.
- [21] B. Jancovici and E. Trizac, *Physica A* **284** (2000) 241.
- [22] B. Jancovici, P. Kalinay and L. Šamaj, *Physica A* **279** (2000) 260.
- [23] L. Šamaj, *Physica A* **297** (2001) 142.